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Letter

Analyzing potassium-ion diffusion in aqueous solutions through pulsed-field gradient NMR

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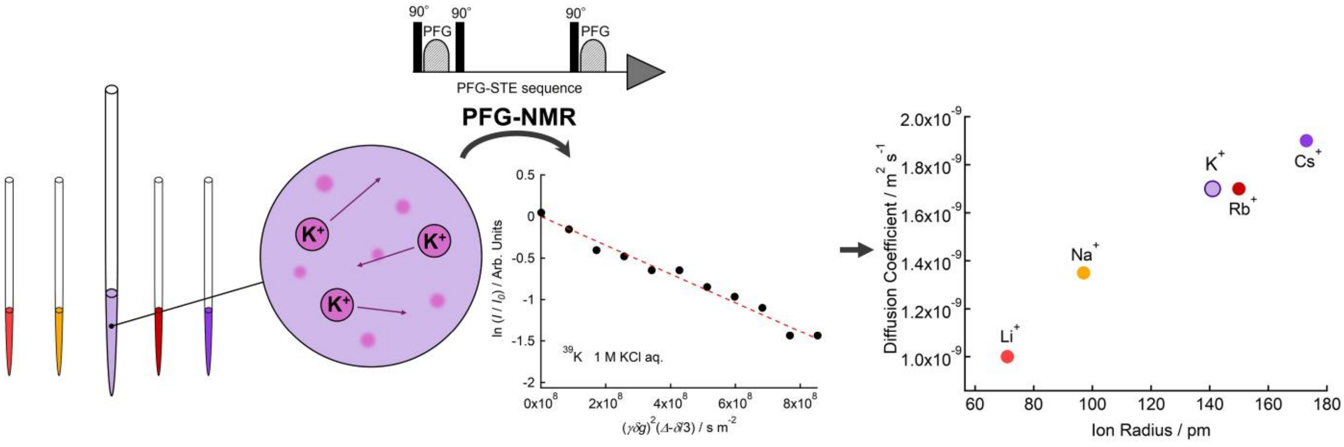
Abstract

The diffusion behavior of potassium ions in aqueous solutions is crucial for advancing both fundamental science and practical applications. Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) is a powerful technique for evaluating ion diffusion. However, its application to potassium has been limited by low Larmor frequency. This study reports the successful measurement of potassium-ion diffusion coefficients in various salt solutions using ^{39}K PFG-NMR through optimizing experimental conditions. The reported data will benefit the development of advanced devices such as potassium-ion batteries.

Keywords: diffusion, potassium, pulsed-field gradient nuclear magnetic resonance.

Graphical Abstract



Alkali metal ions play a central role in various fields, including energy devices[1–4] and biological systems.[5,6] Understanding the diffusion behavior of these ions in solution is crucial for elucidating the mechanisms of chemical reactions and biological functions, as well as for optimizing materials used in electrochemical devices. Conventionally, diffusion coefficients have been evaluated by experimental and computational methods, such as optical techniques, electrochemical measurements, and molecular simulations.[7–11] Among these, pulsed-field gradient nuclear magnetic resonance (PFG-NMR) is a powerful, noninvasive, and direct method for quantifying the diffusion coefficients of target ions. PFG-NMR has been widely used to study the transport of lithium and sodium ions,[12–14] facilitating the development of energy storage devices and enhancing our understanding of biological systems.

Potassium ions also play an important role in various fields, including energy storage devices and biological transport. In particular, potassium-ion batteries have recently attracted attention as promising next-generation batteries, owing to their potential for high energy output and abundance of resources.[3] A comprehensive understanding of potassium-ion diffusion is thus essential for developing advanced energy devices.

Although PFG-NMR is potentially a powerful technique for evaluating potassium-ion diffusion, its application has been limited. This is attributable to the low NMR sensitivity of potassium nuclei, resulting from their extremely low Larmor frequency (23.3 MHz at 11.7 T). Furthermore, only a few commercial NMR probes capable of measuring potassium nuclei. To the best of our knowledge, the first report on potassium PFG-NMR measurements was published by Graham

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Table 1 Parameters used for PFG-NMR measurements of each sample solution.

…	Concentration/M	δ/ms	Δ/ms	g/T m^{-1}	Scans
KCl	1.0	4	45	0.1 to 2.8	1024
KBr	1.0	3	40	0.1 to 2.5	4096
KNO_3	1.0	4	45	0.1 to 2.8	1024
KPF_6	Saturation (0.3 M)	3	40	0.1 to 2.8	1024
KNO_2	1.0	4	45	0.1 to 2.5	1024
	2.5	4	45	0.1 to 2.8	1024
	5.0	4	45	0.1 to 2.8	1024
	Saturation (35 M)	7	50	0.1 to 2.6	128

et al. in 2024,[15] who demonstrated the feasibility of ^{39}K PFG-NMR in concentrated KNO_2 solutions. Subsequently, Wang et al. reported potassium diffusion in biological solutions using exceptionally strong gradient fields (up to 14.54 T m^{-1}) and high magnetic fields (17.6 T).[16] However, systematic data on the diffusion coefficients of potassium ions remain limited. Demonstrating the feasibility of PFG-NMR measurements across various potassium salts and concentrations would significantly enhance our understanding of ion transport and support various applications.

Considering these aspects, this study was aimed at using PFG-NMR to measure potassium-ion diffusion coefficients in various potassium salt solutions and KNO_2 aqueous solutions of various concentrations. All measurements were performed under a static magnetic field of 11.7 T using a custom-built probe with a maximum magnetic field gradient of 3 T m^{-1}. The findings can enable systematic comparison of the fundamental physical properties of alkali metal ions and provide valuable reference data for the development of advanced electrolytes and systems involving complex ion transport.

To prepare the potassium salt solutions, potassium chloride (KCl), potassium bromide (KBr), potassium nitrate (KNO_3), and potassium nitrite (KNO_2) were dissolved in water to achieve a solution concentration of 1.0 M. Additionally, a saturated potassium hexafluorophosphate (KPF_6) aqueous solution was prepared by adding an excess amount of KPF_6 to water. To assess the concentration-dependent behavior, KNO_2 solutions of 2.5, 5.0, and near-saturated (35 M) concentrations were prepared, in addition to the 1.0 M solution. All solutions were transferred to 5 mm NMR tubes for analysis.

For the ^{39}K diffusion NMR experiments, an NMR spectrometer equipped with an 11.75 T magnet (JNM-ECZ500R; JEOL, Japan) was used. A previously reported custom-built diffusion NMR probe[17] was adjusted to the ^{39}K resonance frequency (23.3 MHz) and used together with a field gradient amplifier capable of generating currents up to 30 A. A pulsed-field gradient stimulated echo (PFG-STE) pulse sequence was used for the diffusion experiments. The measurement parameters for each solution are summarized in Table 1. Here, δ denotes the gradient pulse duration, Δ is the diffusion time, and g is the gradient strength. The 90° pulse length was 50 μs, and the relaxation delay was 1 s. Measurements were performed at 303 K. The diffusion measurements were performed at the center of the peak obtained from a single-pulse NMR experiment.

The obtained signal attenuation curves were fitted using the Stejskal–Tanner equation Eq. (1) to calculate the diffusion coefficients: D

$$I(g) = I_0 \exp(-D(\gamma\delta g)^2(\Delta - \delta/3)) \tag{1}$$

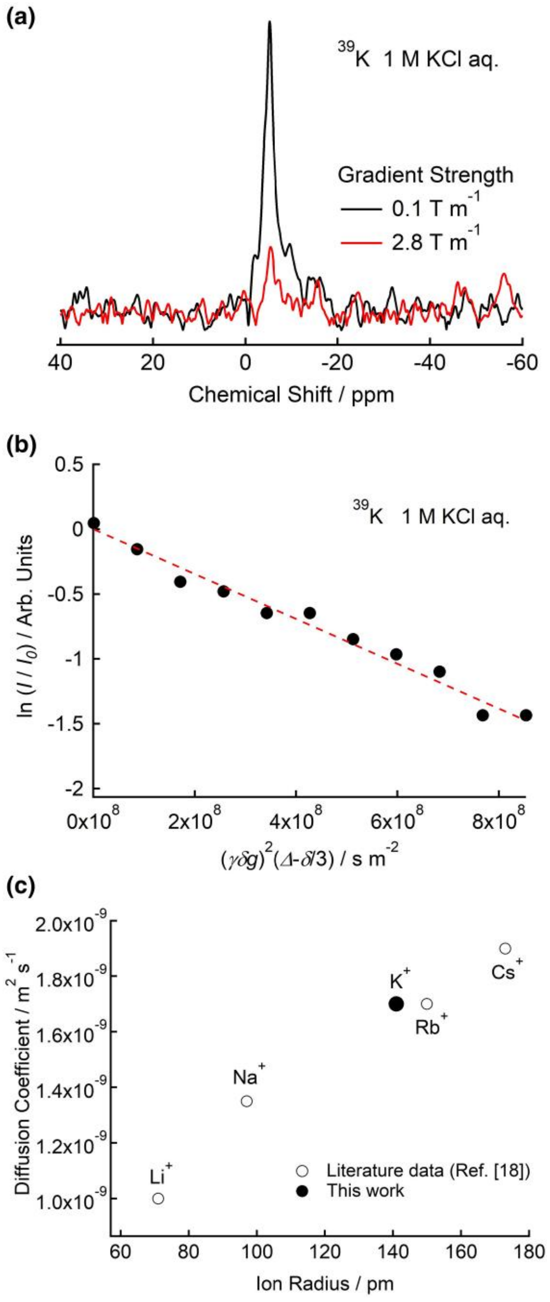

Fig. 1 a) ^{39}K PFG-STE NMR spectra of 1.0 M KCl aqueous solution, b) Diffusion plot of potassium ions in 1.0 M KCl aqueous solution based on the Stejskal–Tanner equation, and c) diffusion coefficients of alkali metal ions as a function of ion radius. The closed circle (●) represents data obtained in this study, whereas open circles (○) represent data from Ref.[18]

where I_0 is the intensity at $g = 0$, and γ is the gyromagnetic ratio (γ for ^{39}K is 1.25×10^7 rad s^{-1} T^{-1}).

Figure 1a shows PFG-STE NMR spectra for potassium ions in 1.0 M KCl aqueous solution measured at gradient strengths of 0.1 and 2.8 T m^{-1}. The corresponding diffusion plot, covering the range from 0.1 T m^{-1} to 2.8 T m^{-1} and based on the Stejskal–Tanner equation, is shown in Fig. 1b. The diffusion coefficient at 303 K was estimated to be 1.7×10^{-9} m^2 s^{-1}. Figure 1c compares the diffusion coefficient of potassium ions obtained in this study with reported values for other alkali metal ions (measured by Hayamizu et al. using

Table 2 Experimental values of potassium diffusion coefficients in each aqueous solution.

…	Concentration/M	K^+ Diffusion Coefficient/$m^2\ s^{-1}$
KCl	1.0	1.7×10^{-9}
KBr	1.0	1.8×10^{-9}
KNO_3	1.0	2.4×10^{-9}
KPF_6	Saturation (0.3 M)	2.7×10^{-9}
KNO_2	1.0	1.9×10^{-9}
	2.5	1.9×10^{-9}
	5.0	1.8×10^{-9}
	Saturation (35 M)	5.5×10^{-10}

PFG-NMR).[18] Although the Stokes radius theoretically correlates with the diffusion coefficient, its determination can be complicated. Therefore, the ion radius was placed on the horizontal axis. The reported diffusion coefficients for other alkali metal ions (Li^+, Na^+, Rb^+, and Cs^+) are 1.0×10^{-9}, 1.35×10^{-9}, 1.7×10^{-9}, and 1.9×10^{-9} $m^2\ s^{-1}$, respectively. In general, these values increase with the ion radius. The measured value for potassium is consistent with that predicted using the trends observed for the other alkali metal ions. The values for rubidium and cesium are slightly smaller than the expected trend. This phenomenon is likely attributable to the difference in the counter anions used for the measurement. Specifically, data for lithium, sodium, and potassium were obtained using chlorides, whereas those for rubidium and cesium were obtained using carbonates. This consistency supports the reliability of our experimental results.

In addition to 1.0 M KCl solution, the diffusion coefficients of potassium ions were also measured in 1.0 M aqueous solutions of KBr, KNO_3, and KNO_2. The estimated diffusion coefficients were 1.8×10^{-9}, 2.4×10^{-9}, and 1.9×10^{-9} $m^2\ s^{-1}$ (Table 2). The diffusion coefficient in saturated KPF_6 aqueous solution was estimated to be 2.7×10^{-9} $m^2\ s^{-1}$. The large value observed for KPF_6 is likely attributable to its low concentration (approximately 0.3 M) even at saturation. These results demonstrate that PFG-NMR can yield reliable diffusion coefficients of the order of 10^{-9} $m^2\ s^{-1}$ for various potassium salts. This confirms the potential of PFG-NMR as a promising technique for measuring potassium nuclei.

The diffusion coefficients of potassium ions in KNO_2 aqueous solutions of various concentrations were estimated using PFG-NMR measurements (Table 2). Figure 2 shows the concentration dependence of potassium diffusion coefficients in KNO_2. Previously, Graham et al.[15] successfully measured the diffusion coefficient of potassium in a 2.5 M KNO_2 aqueous solution using PFG-NMR.[15] In contrast, this study evaluated the diffusion coefficients in KNO_2 solutions with concentrations of 1.0, 2.5, 5.0, and 35 M (near-saturated) solutions. No significant difference was observed in the diffusion coefficients at low concentrations (up to 5.0 M). However, the diffusion coefficient decreased with increasing KNO_2 concentration, reaching 5.5×10^{-10} $m^2\ s^{-1}$ at near-saturation. Previous studies for LiCl and NaCl aqueous solutions have reported that the diffusion coefficients of lithium ion and sodium ion decreased with an increase in concentrations.[18] In this study, it was confirmed that potassium ions exhibit behavior similar to that of lithium and sodium. This demonstrates that PFG-NMR can reliably measure the potassium diffusion coefficient across a wide concentration range. The achievements of this study could be particularly useful in the development of potassium-ion batteries. Unfortunately, we were unable to obtain reliable potassium diffusion coefficients in nonaqueous electrolytes under our current experimental conditions due to poor signal attenuation. However, we anticipate that the development of a probe capable of generating stronger magnetic field gradients would allow the measurement of diffusion coefficients in nonaqueous electrolytes as well.

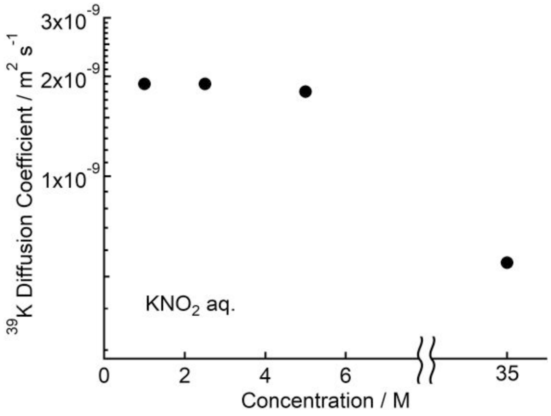

Fig. 2 Concentration dependence of potassium diffusion coefficients in KNO_2 aqueous solutions.

In conclusion, we successfully measured the diffusion coefficients of potassium ions in various potassium salt aquation solutions using ^{39}K PFG-NMR. The measured values were in good agreement with those predicted using the systematic trends of other alkali metal ions, demonstrating the reliability and accuracy of our measurements. The fast diffusion behavior of potassium ions was clearly demonstrated. These results provide valuable experimental data to promote the development of advanced devices such as next-generation batteries. Overall, this study expands the applicability of PFG-NMR to a wider range of alkali metal systems and contributes to a deeper understanding of ion transport phenomena.

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Conflict of interest statement. None declared.

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